LIBRARY
15, No. 1 Dartmouth College
B.

VOL. XV. 1. JANUARY, 1862.

THE

JOURNAL

OF

THE CHEMICAL SOCIETY.

Committee of Publication.

E. FRANKLAND, PH.D., F.R.S. | W. ODLING, M.B., F.R.S.
A. W. HOFMANN, LL.D., F.R.S. | A. W. WILLIAMSON, PH.D., F.R.S.

Editor:

HENRY WATTS, B.A., F.C.S.

N° LVII.

HIPI ((Dartmouth Coll. Library.)) EET.

Received

CHEMICAL SOCIETY.

Officers and Council.

Elected March 30, 1861.

PRESIDENT.

A. W. HOFMANN, LL.D., F.R.S.

VICE-PRESIDENTS,

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

W. T. BRANDE, F.R.S.
B. C. BRODIE, F.R.S.
C. G. B. DAUBENY, M.D., F.R.S.
THOMAS GRAHAM, F.R.S.
W. A. MILLER, M.D., F.R.S.
LYON PLAYFAIR, PH.D., C.B., F.R.S.
COLONEL PHILIP YORKE, F.R.S.

VICE-PRESIDENTS.

H. BENCE JONES, M.D., F.R.S.
ROBERT PORRETT, F.R.S.
ALFRED SMEE, F.R.S.
A. W. WILLIAMSON, PH.D., F.R.S

SECRETARIES.

THEOPHILUS REDWOOD, PH.D.
WILLIAM ODLING, M.B., F.R.S.

FOREIGN SECRETARY.

E. FRANKLAND, PH.D., F.R.S.

TREASURER.

WARREN DE LA RUE, PH.D., F.R.S.

OTHER MEMBERS OF THE COUNCIL.

THOMAS ANDREWS, M.D., F.R.S.
WILLIAM FRANCIS, PH.D., F.L.S.
J. H. GLADSTONE, PH.D., F.R.S.
G. D. LONGSTAFF, M.D.
W. MARCET, M.D., F.R.S.
JOHN MERCER, F.R.S.
A. R. NORMANDY, ESQ.
W. H. PERKIN, ESQ.
H. E. ROSCOE, PH.D.
EDWARD SCHUNCK, PH.D.
JOHN STENHOUSE, LL.D., F.R.S.

LIBRARIAN.

HENRY WATTS, B.A., F.C.S.

COLLECTOR.

MR. THOMAS WEST, BURLINGTON HOUSE.

JOURNAL

OF

THE CHEMICAL SOCIETY

I.—*On Sparteine.*

By E. J. Mills.

The formula of Sparteine, the volatile base discovered by Stenhouse,* in *Spartium scoparium*, has long been a matter of doubt among chemists. Stenhouse assigns to this substance the composition—

$$C_{15}H_{13}N‡$$

which expression cannot be represented if the carbon-equivalent (C=12) be adopted. To avoid this difficulty, Gerhardt† proposed the formula—

$$C_{16}H_{13}N,‡$$

which offered a tolerable approximation to the analytical results of Stenhouse, without, however, deciding the question by an appeal to experiment. The opinion of this illustrious chemist, so often tried and found correct in similar cases, has, very naturally, been accepted in most Manuals. Nevertheless, the point remained unsettled; and it appeared of some interest to gain additional experimental eivdence for the final elucidation, not only of the formula, but also of the constitution of sparteine. Some results which I have obtained in this direction, are recorded in the following paragraphs:

In preparing this substance, I have essentially followed the process devised by Dr. Stenhouse. The plant was simply

* Stenhouse, Ann. Ch. Pharm. (1851), lxxviii, 15.

† Gerhardt. Chim. org. iv, 236.

‡ (C = 6, O = 8, &c.)

exhausted with water faintly acidulated with sulphuric acid. The extract was then evaporated to a smaller bulk, and distilled with caustic soda until the distillate ceased to exhibit a bitter taste or an alkaline re-action. On evaporating the distillate, mixed with hydrochloric acid, to dryness on the water-bath, and distilling the mass with solid hydrate of potassium—the mixture being just moistened at the commencement—the thick, oily base passed over into the receiver,—long preceded, of course, by the ammonia invariably present. The substance was then gently heated with sodium, in a current of dry hydrogen gas, by which means all the water was removed. (It deserves to be noticed that no other mode of drying succeeded; even exposure *in vacuo* for twenty-four hours, with metallic sodium, failed to dehydrate the base.) The sparteine was now freed from the sodium and again distilled, the assistance of the current of hydrogen being this time dispensed with. 150lbs. of the plant yielded about 22 cub. cent. of base.

I need not recapitulate the properties of this substance, already so well described by Stenhouse. If its high boiling point be considered, the idea naturally suggests itself to attribute a diammonic character to sparteine. This circumstance, together with the odour, the well-defined narcotic action, and other properties, tempted me to hope that it would prove homologous with nicotine. In fact, if Gerhardt's formula be doubled, the homology of the two substances, which are so closely allied in their chemical characters, becomes at once apparent.

Nicotine, $C_{10}H_{14}N_2$* Sparteine, $C_{16}H_{26}N_2$.

In this hope, however, I was disappointed, as will be seen from the following numbers:—

I. 0·32475 grm. substance, burnt with oxide of copper, gave 0·91525 grm. carbonic acid and 0·33375 grms. water.

II. 0·4225 grm. substance, again distilled and similarly treated, gave 1·18675 grm. carbonic acid, and 0·43625 grm. water.

	I.	II.
Carbon . .	76·86	76·86
Hydrogen .	11·42	11·47
Nitrogen .	,,	,,

These results are so closely coincident with those of Dr. Sten-

* C = 12, &c., et seq.

house that they may be fairly assumed to represent the composition of sparteine, which would thus become a diamine, containing—

$$C_{15}H_{26}N_2$$

a formula which is unequivocally supported by its deportment with iodide of ethyl.

The following table shows the theoretical values of Gerhardt's and Stenhouse's formulæ, together with the means of the analytical results obtained by Stenhouse and myself respectively:

Gerhardt's Formula (doubled).		Stenhouse's Formula (doubled).		Stenhouse. (Analysis).	Mills. (Analysis).
C_{16}	78·05	C_{15}	76·92	76 69	76·86
H_{26}	10·57	H_{26}	11·11	11·09	11·44
N_2	11·38	N_2	11·97	,,	,,

Salts of Sparteine.

Some of these salts are uncrystallizable, while others are easily obtained in crystals.

The *chloride, bromide,* and *iodide* are amorphous, of a resinous character, and unfit for analysis.

The *oxalate* I obtained by neutralizing the aqueous solution of the base with oxalic acid and evaporating. The crystals were of acicular form, and difficult to obtain.

For additional corroboration of the formula of sparteine, I have examined several of its double-salts.

Platinum-salt.—This salt is precipitated as a yellow crystalline powder, when a solution of dichloride of platinum is added to a solution of sparteine in hydrochloric acid. It may be readily purified by solution in hot hydrochloric acid, filtering, and recrystallizing. With care, large crystals, having very brilliant faces, may be obtained. Analysis furnished the following numbers:—

I. 0·475 grm. substance, dried *in vacuo*, gave, on combustion, 0·459 grm. carbonic acid, and 0·2105 grm. water.

II. 0·613 grm. same substance, similarly dried, gave, on ignition, 0·176 grm. platinum.

III. 0·4795 grm. substance, similarly dried, gave, on combustion, 0·4795 grm. carbonic acid, and 0·2280 grm. water.

IV. 0·45175 grm. substance, dried at 100°, gave, on ignition, 0·1317 grm. platinum.

V. 0·34750 grm. substance, dried at 100°, gave, on ignition, 0·10250 grm. platinum.

These numbers lead to the formula—

$$C_{15}H_{26}N_2.2HCl.2PtCl_2+2H_2O$$

the theoretical values of which I place in juxtaposition with the experimental percentages:—

	Stenhouse.				Mills.				
	I.	II.	III.	IV.	I.	II.	III.	IV.	V.
Carbon .	26·55	26·33	„	„	26·35	„	27·01	„	„
Hydrogen	4·99	4·74	„	„	4·92	„	5·28	„	„
Platinum	29·02	28·63	28·73	28·75	„	28·71	„	29·16	29·49

		Theory.	
C_{15}	=	180·00	26·38
H_{32}	=	32·00	4·69
N_2	=	28·00	4·11
Cl_6	=	213·00	31·22
Pt_2	=	197·40	28·91
O_2	=	32·00	4·69
		682·40	100·00

The *Gold-salt* was prepared, but not analysed, by Stenhouse. I have obtained this salt with all the properties assigned to it by its discoverer.

0·188 grm. substance gave, on ignition, 0·0605 grm. gold = 32·18 per cent. This number agrees with the formula—

$$C_{15}H_{26}N_2.2HCl.AuCl_3$$

which requires 32·27 per cent.; and thus it is seen that the hydrochlorates of the diamines are capable of combining, either with one or with two equivalents of a metallic chloride.

I have also prepared the *zinc-iodide* and *zinc-chloride* of sparteine. They are readily obtained by gently heating a solution of sparteine with hydriodic acid and iodide of zinc, or with hydrochloric acid and chloride of zinc.

Iodide of Zinc and Sparteine.—This salt crystallizes in fine needles, which are apt to become brown on exposure to air. I have only determined the iodine in this salt.

0·366 grm. substance, dried *in vacuo*, and precipitated with nitrate of silver, gave 0·4225 grm. of iodide of silver = 62·39 per cent. iodine. The formula—

$$C_{15}H_{26}N_2.2HI.2ZnI$$

requires 62·78 per cent.

Chloride of Zinc and Sparteine.—This salt crystallizes in magnificent needles, which I have obtained half an inch long. They are white, somewhat hard, and lustrous. The composition of this salt is probably

$$C_{15}H_{26}N_2.2HCl.2ZnCl.$$

Action of Iodide of Ethyl on Sparteine.

The process of ethylation, unknown at the time when sparteine was first prepared, has proved of the greatest service in establishing the constitution of this base.

When equal volumes of sparteine, ordinary methylated spirit, and iodide of ethyl, are heated together for about an hour, in sealed tubes, at 100° C., the mixture assumes a dark colour, and deposits abundance of crystals of an ethylated compound,—sparingly soluble in cold, readily soluble in hot alcohol, and excessively soluble in water. Well-washed with cold, and once recrystallized from hot alcohol, the substance was obtained pure, and gave the following analytical results:—

I. 0·5010 grm. substance* gave, on combustion with a mixture of chromate of lead and oxide of copper, 0·7275 grm. carbonic acid, and 0·2895 grm. water.

II. 0·4550 grm. substance, similarly treated, gave 0·6505 grm. carbonic acid, and 0·2635 grm. water.

III. 0·5135 grm. substance, gave, on precipitation with nitrate of silver, 0·4656 grm. iodide of silver.

IV. 0·31525 grm. substance gave, on similar treatment, 0·2861 grm. iodide of silver.

These numbers represent the formula

$$C_{17}H_{32}N_2I_2 = [C_{15}H_{27}(C_2H_5)N_2]''I_2,$$

* The substance was in each analysis, dried in vacuo.

as may be seen from the following comparison of the theoretical values with the experimental percentages :—

		Theory.		Experiment.			
				I.	II.	III.	IV.
C_{17}	=	204	39·38	39·60	38·99	,,	,,
H_{32}	=	32	6·18	6·42	6·43	,,	,,
N_2	=	28	5·40	,,	,,	,,	,,
I_2	=	254	49·04	,,	,,	49·00	49·04
		518	100·00				

The formation of this compound proves most satisfactorily the diammonic nature of sparteine.* The iodide crystallizes in the form of long needles, beautifully grouped, and radiating from a centre. Treated with a boiling solution of potash, this salt remains unaltered; oxide of silver, however, rapidly transforms it, when in aqueous solution, into the powerfully alkaline hydrated oxide—

$$\left.\begin{matrix}[C_{15}H_{27}(C_2H_5)N_2] \\ H_2\end{matrix}\right\} O_2$$

the composition of which was confirmed by the analysis of its *platinum-salt*. This was prepared by treating the iodide with chloride of silver, and the chloride thus produced with dichloride of platinum, in the *cold*. In this manner, a semi-crystallized precipitate was obtained, soluble in water, alcohol, and more readily in hydrochloric acid. Dried *in vacuo* over sulphuric acid :

0·227 grm. substance gave, on ignition, 0·066 grm. platinum, corresponding to 29·07 per cent. The formula

$$C_{17}H_{32}N_2Pt_2Cl_6 = [C_{15}H_{27}(C_2H_5)N_2]Cl_2.2PtCl_2$$

requires 29·26 per cent.

* Note. In the above reaction between iodide of ethyl and sparteine, a secondary product is found, in very small quantity, in the alcholic washings from the monoethylated di-iodide. The substance is white, excessively soluble in alcohol, almost insoluble in cold, sparingly soluble in hot water. Crystallized from the latter solvent, it appears in the form of small, well-defined, almost square rhombohedral crystals. I determined the iodine in this substance, as well as the platinum in the platinum-salt obtained from it; the numbers were respectively 36·25 per cent. (I), and 27·95 per cent. (Pt). It will be perceived that these numbers present a mutual discrepancy; and I much regret that I was unable to procure sufficient substance for a determination of the carbon and hydrogen.

The *dichloride* corresponding to the mono-ethylated di-iodide, is less easy to obtain, and crystallizes also in needles. It forms, with chloride of zinc, a beautiful acicular double salt, easy to crystallize.*

Action of Iodide of Ethyl on Ethyl-Sparteine.

When the hydrate of this base, obtained by the action of oxide of silver on the iodide, is digested with alcohol and iodide of ethyl in sealed tubes, at 100° C., for a short period, there is obtained, on evaporation of the liquid, a crystalline iodide, always contaminated with free iodine, which differs essentially from the iodide of the mono-ethylated base. If the evaporation be conducted in a stream of sulphuretted hydrogen gas, the separation of much of the iodine is effected, and the substance rendered considerably purer. The new iodide crystallizes from alcohol in short minute crystals, and is very soluble in water. Treated with oxide of silver, it yields a powerfully alkaline solution. Boiled with chloride of silver, the iodide is converted into the corresponding chloride, which is deliquescent, and not easy to obtain in crystals. The latter, treated with dichloride of platinum, furnishes a very voluminous platinum-salt of light yellow colour, and crystallizing in radiated aggregations from its solution in weak alcohol. It is very soluble in water; a mixture of alcohol and ether fails to precipitate it entirely. On analysis,

0·213 grm. substance gave, by ignition, 0.0610 grm. platinum = 28·64 per cent.

Want of material here prevented me from performing these experiments on a more extensive scale. The natural interpretation of the above observations would be to assume that the action of iodide of ethyl upon the mono-ethylated sparteine produces the di-ethylated iodide—

$$C_{19}H_{36}N_2I_2 = [C_{15}H_{26}(C_2H_5)_2N_2]''I_2,$$

which, with oxide of silver, yields the caustic hydrate of the diammonium—

$$C_{19}H_{38}N_2O_2 = [C_{15}H_{26}(C_2H_5)_2N_2]'' \left.\begin{matrix} \\ H_2 \end{matrix}\right\} O_2$$

* Compare Dr. Hofmann's "Notes of Researches on the Poly-ammonias." No. XIV. "Diagnosis of Diamines."—Proceedings of Royal Society, vol. xi, p. 278.

furnishing, lastly, by treatment with hydrochloric acid and dichloride of platinum, the platinum-salt—

$$C_{19}H_{36}N_2Pt_2Cl_6 = [C_{15}H_{26}(C_2H_5)_2N_2]''Cl_2.2PtCl_2.$$

This formula requires 28·10 per cent. of platinum. The analysis above gives as much as 28·64 per cent. The salt was probably still contaminated with a minute proportion of the mono-ethylated compound.

The results of this inquiry prove unmistakably that sparteine is a tertiary diamine of the formula

$$C_{15}H_{26}N_2 = (C_{15}H_{26})^{vi}N_2.$$

Further investigation is necessary to afford some insight into the nature of the complex atom $(C_{15}H_{26})^{vi}$ which assumes the place of six equivalents of hydrogen.

The above experiments on sparteine were carried out in Dr. Hofmann's laboratory.

II.—*On the occurrence of deposits of Crystallised Phosphate of Lime in Human Urine.*

By H. Bence Jones, M.D., F.R.S., F.C.S.

In March, 1861, Dr. William Roberts, Physician to the Manchester Royal Infirmary, published a paper, in the British Medical Journal, on the occurrence of deposits of crystallised phosphate of lime in human urine. He says:—"By adding a little chloride of calcium to healthy urine, and reducing its acidity to near the neutral point with caustic soda, I have often succeeded in obtaining an abundance of crystals, closely resembling those occurring spontaneously in urine."

At this date I had satisfied myself, that healthy urine, out of the body, could be made to give crystals of phosphate of lime, first, by simply adding chloride of calcium to the urine; secondly, by taking away some of the acidity of the urine; thirdly, by both means simultaneously.

When the fluid was very acid, much chloride of calcium was required to be added; but if a portion of the acid was removed in

any way, then less chloride of calcium was required to produce crystals of phosphate of lime.

These experiments made me believe, that, by giving a lime-salt internally, phosphate of lime crystals ought to be found in the urine, even without adding anything to the water after it was made.

A long delay occurred before I could begin the observations in St. George's Hospital, and ultimately I was obliged to ask my friend, Dr. Dickenson, to undertake the microscopical examination of the urine of those to whom the lime-salt was given.

Although, therefore, these experiments were ended long after Dr. Roberts' publication, yet, as the observations recorded in the first part of this paper, were made without any knowledge that he was experimenting on the same subject, our agreement must be considered as accidental, and may therefore be taken as the better evidence of the truth of our facts.

PART 1. *On the production of crystals of Phosphate of Lime in the Urine, by the addition of substances after it has been passed.*

IT appeared desirable to determine the circumstances and form in which crystallised phosphate of lime occurred, when pure solutions of chloride of calcium, and common phosphate of soda, or acid phosphate of soda were mixed together.

When a solution of chloride of calcium in excess is precipitated by a solution of common phosphate of soda, the precipitate, when examined by the microscope, is seen to be partly amorphous and partly crystalline. The amorphous precipitate, according to Heintz, is $3CaO.\ PO_5$, and the crystalline $2CaO.HO.PO_5$.

When a solution of common phosphate of soda, in excess, is precipitated by solution of chloride of calcium, the precipitate, examined by the microscope, is amorphous.

If a little acetic acid is first added to the solution of common phosphate of soda, and then the solution of chloride of calcium, an amorphous precipitate is first seen, and this, more or less rapidly (in the course of half an hour) becomes entirely crystalline. When lactic acid, butyric acid, valeranic acid, or very weak hydrochloric acid was used instead of acetic acid, the same crystals were observed after a short time. If an excess of these acids was used, no crystals were formed.

When a solution of chloride of calcium in excess was added to a solution of acid phosphate of soda, crystals of phosphate of lime were found by the microscope, in from ten to fifteen minutes.

When there was much acid phosphate, in proportion to the chloride of calcium, the crystalline deposit was always found.

It was clear then that crystalline phosphate of lime was formed, if sufficient lime-salt was present, and if the acid was not in such excess as to keep the salt dissolved.

As the urine always contains common phosphate of soda or acid phosphate of soda, with or without free acid, and with variable quantities of lime-salt, experiments were made to obtain crystalline phosphate of lime, 1st, by increasing the lime-salt by adding chloride of calcium; or, 2ndly, by diminishing the acidity of the urine by cautious additions of alkali, so as to allow the lime-salt naturally present to crystallise out; or, 3rdly, by increasing the lime-salt, and diminishing the acidity of the urine at the same time. In each of these ways, crystals of phosphate of lime were obtained.

1st. By simply adding chloride of calcium to healthy urine.

To 50 c. c. of urine, a few drops of a strong solution of chloride of calcium were added, until a slight precipitate was obtained. The precipitate that formed, was first amorphous, but half an hour afterwards, beautiful crystals of phosphate of lime were seen by the microscope. If a great excess of chloride of calcium was added, the precipitate was almost entirely amorphous.

Thirteen different experiments were made with different healthy urines from two men, chloride of calcium in solution was added, and in each case, crystals of phosphate of lime were found in from half an hour to an hour.

2ndly. Crystalline phosphate of lime was obtained from healthy urine, by diminishing the acidity of the urine by the cautious addition of alkali.

To 30 c. c. of healthy urine, a quantity of ammonia was added, not sufficient to produce a precipitate. After standing 12 hours, no crystals of phosphate of lime could be found with the microscope.

To 30 c. c. of urine, ammonia was added, so that the urine had a feebly acid reaction. The precipitate which formed, appeared, when examined by the microscope, to consist chiefly of crystallised phosphate of lime.

To 30 c. c. of urine, so much ammonia was added, as gave a neutral reaction. Besides crystals of phosphate of ammonia and magnesia, crystals of phosphate of lime were formed.

In another experiment, the urine was made alkaline; the precipitate then consisted of phosphate of ammonia and magnesia, and amorphous phosphate of lime.

Solution of common phosphate of soda, and solution of potassa also, when added to healthy urine, occasionally gave, on standing for some time, crystals of phosphate of lime.

3rdly. By increasing the lime-salt, and diminishing the acidity of the urine at the same time, crystalline phosphate of lime was produced.

Four specimens of healthy urine gave with chloride of calcium, no precipitate. Solution of potassa was then added in small quantity till a slight precipitate was observed; the urine still had a slightly acid reaction; on examination with the microscope from half an hour to an hour afterwards, crystals of phosphate of lime were found.

In two other cases, some of the acidity was removed by potassa, and solution of chloride of calcium was then added; the precipitate, when examined with the microscope, contained crystals of phosphate of lime.

In another case in which chloride of calcium gave no precipitate at all, the urine was mixed with a little ammonia to take away the greater part of the acid present, and then a solution of chloride of calcium was added. The precipitate contained crystals of phosphate of lime.

That it is not necessary to lessen the acidity of the urine, provided the phosphate of lime is in great excess, is proved by the following experiments:—

To 50 c. c. of healthy urine, a few drops of, 1st, dilute acetic, or 2ndly, lactic acid, were added, and then so much of a solution of chloride of calcium as caused only a slight precipitate. After standing some hours, the precipitate, which was at first amorphous, was changed in both cases into beautiful crystals of phosphate of lime.

Hence—

The two chief conditions, which need not co-exist, on which the formation of crystalline phosphate of lime in the urine depends, are—

1st. An excess of phosphate of lime; and

2ndly. A slight acidity of the urine, in which the phosphate of lime is dissolved.

PART 2.—*On the production of Crystals of Phosphate of Lime in the urine by giving preparations of lime as medicine.*

THE ease with which crystals of phosphate of lime were obtained after any urine was passed, by adding substances to the urine, led me to expect, that by giving lime-salts as medicine, phosphate of lime crystals would, with equal readiness, be detected in the urine.

I soon found that it was not so easy to affect the composition of the urine before it passed from the body, and that careful collecting, and watching for many hours afterwards, was required to arrive at clear results.

My friend, Dr. Dickenson, undertook the microscopical examination of the urine in the wards of St. George's Hospital, where I ordered the preparations and quantities of the medicine which I wished to try.

At first, acetate of lime with lime-water, and sometimes with carbonate of potassa, to reduce the acidity of the urine, were tried. Then lime-water alone, or carbonate of lime was used; but ultimately a solution of acetate of lime, containing about 15 grains to a drachm of solution, gave the best results.

As examples of our first experiments, we give the following,—

E. P., æt. 22, admitted May 15, 1861, for dyspepsia. He was nearly leaving the hospital well, and the urine was healthy, and in all respects natural, when he was ordered, June 1st, 2 drachms of solution of acetate of lime, in water every six hours, (each drachm contained 14·7 grains of acetate of lime). The urine which was passed at night and morning was repeatedly examined, after standing for various periods, but nothing but a few crystals of oxalate of lime was observed.

On the 4th, eight ounces of lime-water were given in the day, instead of the acetate.

On the 6th, still only oxalate was found. The lime-water was increased to a pint.

On the 8th, a drachm of carbonate of potassa in addition was given.

On the 11th, no change having been observed, the morning urine was faintly acid; and the surface was covered with an iridescent plate of phosphate of lime. The evening urine was faintly acid when passed, and no crystals of phosphate of lime were found at first. It was again examined forty hours afterwards;

it was then alkaline, and a white precipitate had fallen, which consisted of a considerable quantity of amorphous phosphate, with a great number of very characteristic crystals of phosphate of lime. The surface was covered with a phosphatic pellicle.

12th and 13th, morning and evening. No crystals of phosphate.

14th. Morning urine alkaline, with phosphatic pellicle, and much deposit, consisting chiefly of amorphous phosphate, with a few stellate crystals of phosphate of lime.

14th, evening urine. Eighteen hours after it was passed, no deposit was found; on the third day, many stellate crystals of phosphate of lime were found.

The experiment was continued until the 20th; phosphate of lime crystals occasionally, but by no means constantly, appearing; oxalate of lime was always detected when the urine was acid.

H. E., æt. 30, admitted May 15th for dyspepsia.

June 1st. The urine was in all respects natural; he drank a pint of lime-water during the day.

June 2nd. A few crystals of phosphate of lime were found.

„ 3rd. No phosphate of lime; some oxalate.

„ 4th. No phosphate of lime crystals were found.

In more than one case, carbonate of lime was given in considerable quantity, but no crystals of phosphate of lime were detected in the urine; but the results with acetate of lime, in large doses, were very decided and very uniform, for example,—

S. K., æt. 24. admitted with chronic rheumatism, July 10.

July 20. The urine was perfectly natural, except a small quantity of pus cells, the result of a gonorrhœa.

He was ordered two drachms of solution of acetate of lime equal to 29·4 grains, in water three times daily.

The urine was examined night and morning, and no crystals, except a few oxalate of lime octahedra, were seen, until—

23rd evening. The urine was faintly acid, with an iridescent pellicle on the surface, and a heavy white precipitate formed, which consisted of amorphous phosphate, oxalate of lime, and very numerous characteristic crystals of phosphate of lime. Three drachms of the solution of acetate of lime were ordered thrice daily.

24th morning. Urine faintly alkaline; amorphous and laminar phosphate of lime were seen, but no crystals of phosphate of lime.

24th evening. Urine acid; very large crystals of oxalate were seen; no phosphate. Four drachms of the solution of acetate of lime were ordered.

25th morning. The urine was acid, and showed a few phosphate crystals.

25th evening. The urine was acid, and showed a large deposit of octahedra, but no phosphate.

26th morning. The urine was acid, but showed no crystals.

26th evening. The urine was very faintly acid; numerous fine crystals of phosphate of lime were found.

July 27, morning. The urine was faintly acid; crystalline phosphate of lime was seen, and much oxalate. The acetate of lime was ordered to be stopped, and only three doses were taken between the 27th of July and the 3rd of August; during which time, crystals of phosphate of lime were only twice found by the microscope.

August 2. Morning urine slightly acid; no phosphate crystals.

„ Evening urine acid; much oxalate but no phosphate. Three drachms of the solution of acetate of lime were ordered in water.

3rd. Night water alkaline; few small phosphate of lime crystals were found.

4th. Morning urine alkaline, and few phosphate of lime crystals were found.

4th. Evening urine alkaline; abundant and splendid crystals of phosphate of lime.

5th. Morning urine faintly acid. Phosphate of lime crystals were found; the experiment was stopped.

L. B., æt. 26, admitted with slight rheumatism, July 10.

July 23. The urine was acid and perfectly natural, except that it contained a quantity of pus cells, the result of gonorrhœa.

Two drachms of solution of acetate of lime equal to 29·4 grains, were given thrice daily. The urine was examined night and morning: no crystals were seen until

24th evening. Urine faintly acid; a few needles of phosphate of lime were found, and much amorphous phosphate.

25th. Three drachms of the solution were ordered, but no more crystals of phosphate of lime were seen until

27th morning. The urine, after standing 48 hours, gave many fine bundles of phosphate of lime crystals.

27th evening. Urine gave much oxalate, but no phosphate.

28th morning. Urine faintly alkaline; gave many fine crystals of phosphate of lime.

28th evening, and 29th morning. The urine was not kept.

29th evening to 31st. When the acetate of lime was omitted, no crystalline phosphate was found.

August 3. Three drachms of the solution were again given thrice daily.

No crystals were found until the evening of the 7th, when the urine was acid, and many phosphate of lime crystals were seen.

Four drachms of the solution were ordered, but the patient disliking the medicine, the experiment was stopped.

C. W., æt. 30, was admitted with chronic rheumatism, July 10.

July 30. The urine was acid and perfectly natural, excepting that occasionally a little bladder epithelium was seen.

Three drachms of the solution of acetate of lime were ordered thrice daily, in water. Nothing was observed until

August 3. Morning urine faintly acid; some decided aggregations of phosphate of lime crystals were seen with microscope.

August 3rd, evening. Urine acid but no deposit.

„ 4th, morning. The urine was acid, and showed much oxalate of lime, but no phosphate.

The medicine had to be omitted, in consequence of an increase of rheumatism.

Conclusion.

From the experiments detailed in this paper, it follows that the formation of phosphate of lime crystals in the urine, does not depend upon the amount of phosphoric acid present, but that it does depend, firstly, on the amount of lime in the urine; and secondly, on the acidity of the urine allowing the crystallization to occur.

The increase of lime in the urine, or the diminution of the acidity of the urine, or the simultaneous occurrence of both of these conditions, does not indicate any diseased condition of the body, but may be caused by medicines or by diet.

III.—*Supplementary Note to a Memoir on the power ascribed to the Roots of Plants of rejecting poisonous or abnormal substances presented to them.*

By Charles Daubeny, M.D., F.R.S., M.R.S.A., Foreign Associate of the Royal Academy of Munich, and Professor of Botany, Oxford.

In a memoir read before the Chemical Society in May last, and, since published in the Scciety's Journal,* I intimated my intention of continuing the researches begun last year, "On the power ascribed to the roots of plants, of rejecting poisonous or abnormal substances presented to them;" and as in the experiments therein detailed, the foreign ingredients had been applied to the plants after they had sprung from the ground, in the liquid form, by watering them with the solution, and it was conceivable that some small portion might have adhered to their external surfaces, although none was actually absorbed by the roots,—I this year endeavoured to avoid that source of error, by introducing the salt into the soil before the seed was sown.

The abnormal substances tried were, as before, the earths strontia and baryta in combination with nitric acid,—and the metal arsenic, which, however, was applied, not in the form of arsenious, but of arsenic acid, which latter, being isomorphous with phosphoric acid, might, it was conceived, be substituted for it in the organism of a plant, and thus become assimilated more readily than arsenious acid.

The crops tried were, as on the former occasion, barley and turnips, and in neither of the two did any very marked difference in the quantity of the crops obtained, arise from the application of the salt. If any thing, the advantage seemed to be rather on the side of those portions of the field which had been thus treated.

The crops were severally examined in the same manner as those of the year preceding had been; but in no one of the six cases, three being the samples of turnips tried with arsenic, baryta and strontia, and three, those of barley treated with the same substances, did any indications of the poisonous or abnormal ingredient which had been introduced into the soil, manifest themselves in the resulting crop.

* Vol. xiv, p. 209.

I consider these results as rather more conclusive than those obtained in the preceding year, because the substance experimented with, being incorporated with the soil before the seed had been sown, could hardly fail to get into contact with the roots at some part or other.

The only question that can arise is, whether the quantity administered was in each case sufficient to become appreciable in the plants that had grown in contact with it. In the case of the arsenic, I hardly know how this point could be determined more fully, as a larger dose of the poison would be fatal to the vitality of the plant, and thus the very conditions of the problem would be vitiated. With regard, however, to the strontia and baryta, where this objection does not seem to exist, it might be well to settle the point more conclusively, by trying whether the earth would be taken up when quantities of either, larger than were this year employed, had been introduced into the soil.

IV.—*On Piperic and Hydropiperic Acids.*

By G. C. Foster, B.A.

Piperic acid was first described in 1857 by v. Babo and Keller.* Their analyses led them to represent its composition by the formula $C_{26}H_{12}O_8$, $C_{50}H_{24}O_{16}$, or $C_{50}H_{22}O_{16}$: the last formula they considered the most probable. The analysis of the acid and of its silver-salt was soon afterwards repeated by Strecker†, who gave the formula $C_{24}H_{10}O_8$ for piperic acid, and the formula $C_{24}H_9MO_8$ for the piperates, and showed that many of Babo and Keller's own analyses agreed with these expressions. If the accuracy of Strecker's formula be admitted, it seems to indicate that piperic acid is a triatomic acid analogous to glyceric acid, $C_3H_6O_4$ ‡; otherwise it is difficult to reconcile its monobasic character with the high proportion of oxygen it contains. These considerations induced me to make a few experiments on piperic acid, in the hope of obtaining some knowledge of the relation in which it stands to bodies whose constitution is better understood.

* J. pr. Chem., lxxii, 53; Jahresber., 1857, p. 413.

† Ann. Ch. Pharm., cv, 317; Jahresber., 1857, p. 414.

‡ Here, and hereafter in this paper, C=12, H=1, O=16.

The piperic acid employed was obtained by decomposing piperine with alcoholic potash, according to Babo and Keller's process; but I found that by employing a closed vessel, in which the materials could be heated above the boiling point of alcohol, much time might be saved: 100 grms. piperine, mixed with an equal weight of solid potash and as much strong alcohol as will dissolve both, is completely decomposed when heated for five or six hours to 100°C.

The analysis of piperic acid and of its potassium- and barium-salts gave me numbers which agree with Strecker's formula, as is shown by the following statement of results.

Piperic acid, $C_{12}H_{10}O_4$.

0·517 grm. acid gave 1·248 grm. carbonic acid and ·229 grm. water.

·443 grm. acid gave 1·074 grm. carbonic acid and ·197 grm. water.

	Calculated.		Found.	
C_{12}	144	66·05	65·83	66·12
H_{10}	10	4·59	4·92	4·94
O_4	64	29·36	,,	,,
$C_{12}H_{10}O_4$	218	100·00		

Piperate of potassium, $C_{12}H_9KO_4$.

0·4371 grm. salt gave ·147 grm. sulphate of potassium.

·425 grm. salt gave ·144 grm. sulphate of potassium.

·7325 grm. salt gave 1·502 grm. carbonic acid and ·232 grm. water.

	Calculated.		Found.		
C_{12}	144	56·25	,,	,,	55·92
H_9	9	3·52	,,	,,	3·52
K	39	15·23	15·08	15·19	,,
O_4	64	25·00	,,	,,	,,
$C_{12}H_9KO_4$	256	100·00			

Piperate of barium, $C_{12}H_9BaO_4$.—This salt was prepared by adding chloride of barium to a solution of piperate of potassium, and purified by crystallization from boiling water, in which it is somewhat more soluble than in cold water, and subsequent wash-

ing with boiling alcohol. A current of carbonic acid passed through a solution of this salt in hot water, decomposes it into carbonate of barium and piperic acid. Air-dry, it does not lose weight at 100°.

0·3082 grm. salt gave ·1251 grm. sulphate of barium.
·3406 grm. salt gave ·1388 grm. sulphate of barium.

	Calculated.	Found.	
Barium per cent. . .	23·99	23·86	23·98

My first experiment with piperic acid was an attempt to reduce it by means of hydriodic acid, in the hope of obtaining a monatomic acid ($C_{12}H_{10}O_2$) which should bear the same relation to it as propionic acid ($C_3H_6O_2$) bears to glyceric acid ($C_3H_6O_4$). In this attempt I was unsuccessful. At 100° C., and even below, piperic acid is converted by hydriodic acid into a black, uncrystallizable substance, carbonic acid being formed at the same time, but no iodine set free. The only crystalline substance which I succeeded in separating from the black carbonaceous product of this reaction, was a small quantity of what appeared to be unaltered piperic acid.

Having failed to reduce piperic acid by hydriodic acid, I hoped to be more successful in employing nascent hydrogen. This reagent, however, instead of giving a product containing less oxygen, gives rise to a new acid containing two atoms of hydrogen more than piperic acid, which I have named *hydropiperic acid*. This substance is best obtained by allowing sodium-amalgam to act for some hours upon a solution of piperate of potassium, kept at a gentle heat, and frequently stirred. The piperate of potassium, which is obtained as a direct product of the action of alcoholic potash on piperine, may be employed for this preparation, after having been once recrystallized. The hydropiperic acid is separated from the alkaline solution by the addition of hydrochloric acid, in the form of oily drops, which gradually solidify when allowed to stand. It may be purified by solution in a large quantity of boiling water, which deposits it on cooling in exceedingly thin, silky needles, sometimes as much as an inch long; or by solution in alcohol, and treatment of the solution with animal charcoal.

Pure hydropiperic acid is colourless; it melts at 63° or 64°C., and solidifies at about 56°; it may sometimes be cooled still lower

without solidifying, but then solidifies suddenly when touched with a glass rod; it does not appear to be volatile without decomposition, but when heated in a test-tube it creeps up the sides of the tube, leaving only a very slight residue at the bottom. It is very slightly soluble in cold water, but sufficiently so to give a faint acid reaction to the solution, and to cause it to give a precipitate with acetate of lead; it is somewhat more, but still only sparingly, soluble in hot water, and gives a solution having a strong acid reaction. It separates on cooling, partly as an oil, partly in very fine crystals. Alcohol dissolves hydropiperic acid in all proportions; in ether, also, it is very soluble, and it crystallizes by the spontaneous evaporation of its ethereal solution, in large, but confusedly formed, hard crystals, apparently belonging to the monoclinic system, and many of them hemitropic.

0·1724 grm. acid gave ·4124 grm. carbonic acid and ·0877 grm. water.

·4885 grm. acid gave 1·1715 grm. carbonic acid and ·2495 grm. water.

·466 grm. acid gave 1·116 grm. carbonic acid and ·235 grm. water.

	Calculated.		Found.		
C_{12}	144	65·46	65·24	65·44	65·31
H_{12}	12	5·45	5·65	5·67	5·60
O_4	64	29·09	,,	,,	,,
$C_{12}H_{12}O_4$	220	100·00			

The first and second analyses were made with the products of two different preparations; the third analysis is of the product obtained by treating some of the same substance as served for the second analysis a second time with sodium-amalgam.

Strong sulphuric acid gives a blood-red colour with hydropiperic acid; fuming nitric acid acts in the same way; nitric acid diluted with its own bulk of water acts violently on hydropiperic acid when slightly heated, giving a solution from which water precipitates a semi-fluid nitro-acid. When hydropiperic acid is heated with excess of alkali, a good deal of gas is given off, and the residue exhibits the reactions of the acid $C_7H_6O_4$, obtained by Dr. Matthiessen and myself*, by distilling hemipinic acid with

* Proc. Roy. Soc., xi, 58.

hydriodic acid, and subsequently obtained by Strecker*, by heating piperic acid with excess of potash. With hydriodic acid it behaves in the same way as piperic acid.

Hydropiperate of ammonium, $C_{12}H_{11}(NH_4)O_4$.—This salt was prepared by neutralizing the acid with ammonia. It crystallizes easily from hot water in small shining scales. For analysis, a portion was dissolved in a little water; the acid was precipitated by hydrochloric acid, collected on a weighed filter, and washed with as small a quantity of water as possible; the filtrate was evaporated; the residue dissolved in very little water; the small additional quantity of acid thus separated was collected on the same filter as before, and the whole quantity weighed, after being dried *in vacuo;* the second filtrate and wash-waters were then again evaporated, and the ammonia was determined in the residue as chloro-platinate.

0·4813 grm. salt gave ·4469 grm. hydropiperic acid and ·4126 grm. chloroplatinate of ammonium.

·5147 grm. salt gave ·4787 grm. hydropiperic acid and ·2146 grm. platinum.

	Calculated.		Found.	
$C_{12}H_{12}O_4$	220	92·83	92·85	93·01
H_3N	17	7·17	6·55	7·16
$C_{12}H_{12}O_4H_3N$	237	100·00	99·40	100·17

A strong solution of hydropiperate of ammonium can dissolve a considerable quantity of hydropiperic acid: the addition of strong aqueous ammonia to such a solution saturated with acid, gives an almost solid mass of hydropiperate of ammonium; by the addition of water, it is decomposed into hydropiperate of ammonium, which dissolves, and hydropiperic acid, which is precipitated.

Hydropiperate of potassium with excess of acid, $C_{12}H_{11}KO_4 + C_{12}H_{12}O_4$.—This salt was obtained by boiling a solution of hydropiperic acid in nearly absolute alcohol with excess of dry carbonate of potassium, filtering the solution while still hot, and allowing it to cool: the salt was thus obtained crystallized in hemispherical clumps of radiating needles. It was analysed after being once recrystallized from alcohol and dried at 100°C.

* Ann. Ch. Pharm., cviii, 280.

0·316 grm. salt gave ·688 grm. carbonic acid and ·1455 grm. water.
0·261 grm. salt gave ·050 grm. sulphate of potassium.

	Calculated.		Found.	
C_{24}	288	60·25	59·38	,,
H_{23}	23	4·81	5·11	,,
K	39	8·16	,,	8·59
O_8	128	26·78	,,	,,
$C_{24}H_{23}KO_8$	478	100·00		

The deficiency of carbon and excess of potassium shown by the analysis were, no doubt, caused by the presence of a small quantity of neutral hydropiperate of potassium (calc. carbon 55·81 per cent.; potassium 15·12 per cent.); indeed, the acid salt appears to be decomposed by repeated crystallization from alcohol into hydropiperic acid and the neutral potassium-salt, at least a portion which had been recrystallized three times from alcohol gave, on analysis, 12·63 per cent. potassium. The acid salt is immediately decomposed by water, with precipitation of hydropiperic acid.

Hydropiperate of calcium, $C_{12}H_{11}CaO_4(+H_2O\,?)$.—Obtained by boiling the acid with milk of lime, filtering hot, and separating the excess of lime by carbonic acid; or by precipitating a rather strong solution of hydropiperate of ammonium with chloride of calcium. This salt is partially decomposed by solution in hot water, but may be purified by crystallization from a mixture of about 2 parts water and 1 part alcohol, which deposits it in bunches of fine needle-shaped crystals. It is only slightly soluble in cold water. The crystals effloresce in the air, but do not lose all their water below about 100° C.; they melt together to a sticky mass at 100°, which may be powdered when quite dry, and then does not again become soft on heating. Hydropiperate of calcium, dried at 100°, does not further diminish in weight at 120°.*

* Hydropiperate of calcium appears to crystallize with one atom of water. A calcium-determination in the air-dry salt gave 7·83 per cent. calcium (the formula $C_{12}H_{11}CaO_4 + H_2O$ requires 7·78 per cent. calcium); after the same salt had stood two days longer over sulphuric acid, it contained 4·2 per cent. water; in other preparations of the salt (air-dry), I found 4·94, 4·88, and 4·87 per cent. water; numbers which do not agree with any simple atomic proportion. The percentage of water calculated for the above formula is 7·00: I can only explain the results obtained, by ascribing them to the rapidity with which the salt effloresces. After drying very quickly, by pressure between paper and exposure to the air, the crystals were found to have partially effloresced when examined under the microscope.

0·595 grm. salt (dried at 105°) gave ·170 grm. sulphate of calcium.

·3348 grm. salt (dried at 100°) gave ·095 grm. sulphate of calcium.

	Calculated.		Found.	
C_{12}	144	60·25	,,	,,
H_{11}	11	4·60	,,	,,
Ca	20	8·37	8·30	8·35
O_4	64	26·78	,,	,,
$C_{12}H_{11}CaO_4$	239	100·00		

Hydropiperate of barium, $C_{12}H_{11}BaO_4$, resembles the calcium-salt, and may be obtained in a similar way. (Found, 23·2 per cent. barium; calculated, 23·8 per cent.)

Hydropiperate of silver, $C_{12}H_{11}AgO_4$.—A crystalline precipitate almost insoluble in cold water; it dissolves in hot water, but is partially decomposed at the same time. It can hardly be dried without undergoing slight decomposition.

0·2933 grm. gave ·0985 grm. metallic silver.

	Calculated.	Found.
Silver per cent. . .	33·03	33·58

A solution of hydropiperate of ammonium gives a whitish brown precipitate with *perchloride of iron*, and white precipitates with *corrosive sublimate*, *mercurous nitrate*, and *acetate of lead*, all of them soluble in hot water.

Hydropiperate of ethyl.—A solution of hydropiperic acid in absolute alcohol was saturated with hydrochloric acid gas, and heated to 130° for four or five hours; the product was then evaporated on a water-bath, and the residue washed with dilute potash. In this way a neutral brown liquid was obtained, which was heavier than, and insoluble in, water. By solution in ether, treatment of the ethereal solution with animal charcoal, and subsequent evaporation, it was obtained as a brownish yellow liquid. It was not altered by dilute potash or ammonia, but gave a half-solid mass, probably *hydropiperamide*, when saturated with gaseous ammonia.

Hydropiperic acid, heated with an excess of monohydrated acetic

acid to 160° C. during 30 hours, appears to be unaltered. The product of this experiment was poured into water, which caused a precipitate of a solid acid; this precipitate was washed to remove acetic acid; about two-thirds of it were then neutralized by lime, the other third added, and the whole evaporated to dryness on a water-bath. The residue was well washed with strong alcohol, the remaining salt crystallized from very dilute alcohol, and then decomposed by hydrochloric acid. The acid thus separated was dried over sulphuric acid, and analysed.

0·3394 grm. acid gave ·810 grm. carbonic acid and ·1724 grm. water. These numbers show that the substance was nearly pure hydropiperic acid, of which it had all the external properties.

	Found.	Hydropiperic acid.
Carbon . . .	65·12	65·46
Hydrogen . . .	5·64	5·45

The deficiency of carbon may, perhaps, indicate that a small quantity of aceto-hydropiperic acid, $C_{12}H_{11}(C_2H_3O)O_4$, (carbon 64·12 per cent.), had been formed.

Hydropiperic acid, heated to 150° C. with chloride of acetyl, gives a neutral oil, insoluble in water and dilute alkalis; probably aceto-hydropiperic anhydride; I do not know whether aceto-hydropiperic acid was formed at the same time or not.

V.—*On the Camphor of Peppermint.*

By A. Oppenheim, Ph.D.

The camphor of peppermint, known as constituting the stearoptene of the essential oil of *Mentha piperita*, has lately been obtained in larger quantities, so as to allow of a closer examination being instituted than has hitherto been possible. It arrives from Japan in coarse earthenware jars, merely protected by paper covers, and consists of a mass of small, white, fragrant, prismatic crystals, resembling sulphate of magnesia, which salt, in fact, seems to be constantly used for the purpose of adulterating the Japanese peppermint-camphor, as from ten to twenty per cent. of that salt may be separated from the camphor by washing it with water. When washed with warm water, the peppermint-camphor melts, and,

on congealing, forms itself into a hard crystalline mass. It melts at 36 C, and distils, without decomposition, at 210°. These properties very nearly coincide with those established by Dumas,* for the stereoptene of American oil of peppermint. The composition of these two substances is exactly the same, viz.:

0·260 grm. of Japanese camphor of peppermint, dried at 100°, gave 0·732 grm. of carbonic acid, and 0·315 grm. of water, or in 100 parts.

	Japan camphor of peppermint.	Dumas American camphor.	Calculated.
C	76·93	76·5	76·92
H	13·40	13·1	12·82
O	„	„	10·26

This corresponds with the formula established by Dumas, $C_{10}H_{20}O$.† Walter verified this formula in 1830, by determining the vapour-density of the corresponding hydrocarbon, $C_{10}H_{18}$.

The nature of this body which, on many grounds, claims our attention, has not been determined by either of these chemists. Whether it be an alcohol, an aldehyde, a ketone, or of a nature less distinct (like the hydrates of oil of turpentine), it possesses particular interest, from the fact of its bordering on the two great groups of organic chemistry, the group of fatty and that of aromatic bodies. To the former it is related by being isomeric with capric aldehyde, and to the latter, by differing from a number of aromatic bodies, merely in the number of its hydrogen-equivalents.

The camphol of Berthelot, $C_{10}H_{18}O$, differs from it by two equivalents of hydrogen; common camphor, $C_{10}H_{16}O$, by four; the cuminic alcohol of Rossi, $C_{10}H_{14}O$, also thymol and carvacrol, by six; and cuminol, $C_{10}H_{12}O$, by eight equivalents of hydrogen.

The relation of camphol and camphor being that of an alcohol and its aldehyde,‡ the position which the camphor of peppermint holds towards them, will call for our particular attention from their being related, not only as regards their composition, but also with respect to their physical properties. The peppermint-camphor turns the plane of polarization to the left.

* Gerhardt, Traité de Chimie Organique, vol. iv. p. 357.

† C = 12; H = 1; O = 16.

‡ Berthelot, "La Chimie Organique fondue sur la Synthèse."

A preliminary determination of its rotatory power has been arrived at by the aid of Dubosc's saccharometer. A tube 22mm. in length was filled with a 10 per cent. solution of peppermint-camphor in alcohol, when it was found to deflect the plane of polarization as much as a plate of quartz 0·44mm. thick. This corresponds to an angle of $10{\cdot}56^\circ = a$, and to a molecular rotatory power,—

$$[a] = \frac{a}{l\epsilon\delta} = 59{\cdot}6.$$

Peppermint-camphor is but slightly soluble in water, although it imparts to the liquid a strong odour and taste. It is very soluble in alcohol, ether, sulphide of carbon, and in fatty and essential oils; insoluble in aqueous solutions of alkalies. From an alcoholic solution of soda, it crystallizes in long needles. A current of sulphurous acid or of hydrochloric acid gas dissolves it. By evaporation, the acids pass off, leaving the peppermint-camphor unaltered. Concentrated acids, especially nitric, sulphuric, hydrochloric, formic, acetic, and butyric acid, dissolve it very freely. From these solutions it is separated by water as well as by alkalies, as an oil which soon solidifies and then exhibits the original properties of the camphor.

When concentrated acetic acid is heated with peppermint-camphor in a sealed tube, for ten or twelve hours, at about 120° C., these two bodies combine into a light oil, no longer decomposible by water or by cold solutions of alkalies. After washing with carbonate of soda, and drying over chloride of calcium, it boils between 222° and 224° C. without decomposition.

I. 0·308 grm. of this distillate yielded, by analysis, 0·314 grm. of water and 0·827 grm. of carbonic acid.

The same body is obtained by the action of anhydrous acetic acid on peppermint-camphor.

II. 0·310 grm. thus prepared, gave 0·303 grm. of water and grm. of carbonic acid.

	I.	II.	Calculated.
C	73·06	72·58	72·73
H	11·04	11·18	11·11

This agrees with the formula,—

$$\left.\begin{matrix} C_{10}H_{19} \\ C_2H_3O \end{matrix}\right\} O.$$

That is, peppermint-camphor in which one equivalent of hydrogen has been substituted by acetyl, so as to form a compound ether.

This body is highly refractive, and deflects the plane of polarization to the left more strongly than the camphor from which it is derived. By preliminary observation with the saccharometer, its molecular rotatory power $[a]$ has been found = 114°. Hydrate of baryta does not seem to decompose it; but, by heating it with an alcoholic solution of soda, to 120° C. for three hours, it is perfectly decomposed into acetate of soda, and an oil which soon congeals into a crystalline mass, not unlike common camphor. After being pressed between blotting-paper, it distils at 210° C., fuses at 34°, and exhibits otherwise the original properties of peppermint-camphor.

Butyric acid combines with peppermint-camphor on being heated with it to 200° C. for about thirty hours.

The product was separated into two parts, distilling from 230° to 240°, and from 240 to 250° respectively. The former of these portions gave the following analytical results:—

0·287 grm. of the liquid gave 0·303 grm. water, and 0·792 grm. of carbonic acid, corresponding to the formula,

$$\left.\begin{matrix} C_{10}H_{19} \\ C_4H_7O \end{matrix}\right\} O,$$

which is that of butyrate of menthyl; in 100 parts,—

	Found.	Calculated.
C	74·84	74·33
H	11·74	11·50

A preliminary determination of its rotatory power gave $[a]$ = 88·80°.

A concentrated solution of hydrochloric acid acts on peppermint-camphor at 100° C. But it is necessary to heat them together for a week in order to obtain a considerable quantity of chloride of menthyl. At a temperature of 120° C., twenty-four hours suffice to complete this reaction.

The chloride of menthyl may be washed with carbonate of soda, but it does not bear distillation. The following analyses were made with non-distilled portions of the liquid dried over chloride of calcium:—

I. 0·323 grm. gave 0·332 grm. of water and 0·794 grm. of carbonic acid.

II. 0·382 grm. gave 0·296 of chloride of silver.

III. 0·310 grm. gave 0·206 grm. of chloride of silver.

This corresponds to the formula $C_{10}H_{19}Cl$, or, in 100 parts,

	I.	II.	III.	Calculated.
C	67·06	„	„	68·62
H	11·32	„	„	10·89
Cl	„	19·16	19·67	20·34

The same body was obtained by Walter, by the action of perchloride of phosphorus on peppermint-camphor.

Iodide and bromide of phosphorus react very strongly on this body; but, as the resulting bodies bear distillation as little as the chloride of menthyl, these methods are not advisable for obtaining them. Hydriodic acid combines with peppermint-camphor at about 120° C.

Sodium acts very strongly on peppermint-camphor. It dissolves therein when fused, and disengages hydrogen. By raising the temperature, about one equivalent of sodium may be made to unite with the fused camphor, forming a vitreous, transparent mass, white originally, but becoming brown and moist when exposed to the air. It is decomposed by water, but soluble in absolute alcohol and in iodide of ethyl. The reaction of this body on the sodium-compound is not so simple as might be expected. When heated to 100°, the transparent liquid solidifies, but continues to be soluble in a mixture of ether and alcohol. From this solution, deliquescent crystals may be obtained, which contain iodine, sodium, carbon, and hydrogen; but continued evaporation decomposes these crystals into iodide of sodium and an oily substance, which does not appear to be the mixed ether expected to be formed by such reaction. The products of this and of similar reactions form the subject of the continuation of these researches.

From the compound ethers and the sodium-compound hitherto obtained, it is already evident that the camphor of peppermint is a monatomic alcohol having the formula—

$$\left.\begin{matrix} C_{10}H_{19} \\ H \end{matrix}\right\} O.$$

It belongs to the general type $C_nH_{2n}O$, and is, therefore, homo-

logous with the allylic alcohol of Hofman and Cahours, and with the acetylic alcohol of Berthelot. As it is isologous with campholic alcohol, the name *mentholic alcohol*, or *menthol*, may perhaps be advantageously substituted for that of camphor of peppermint.

The corresponding hydrocarbon, menthene, $C_{10}H_{18}$, which Walter obtained by the action of phosphoric acid, may likewise be produced in various other ways. It has been found among the products of the reaction of chloride of menthyl on ethylate of sodium. The most advantageous way of preparing it seems to be to react on menthol with chloride of zinc. Prepared in this way, the menthene has no action on polarized light. It boils at 163° C.

0·227 grm. yielded, by analysis, 0·282 grm. of water, and 0·733 grm. carbonic acid; in 100 parts—

	Found.	Calculated.
C	86·59	86·94
H	13·65	13·05

Bromine does not combine directly with this hydrocarbon. It reacts on it very violently, disengaging currents of hydrobromic acid, and forming various products of substitution, of no stability whatever, even at ordinary temperatures.

By adding, drop by drop, two equivalents of bromine to one of menthene, monobrominated menthene $C_{10}H_{17}Br$ must be formed, which, by the action of oxide of silver, or of hydrate of soda, might be transformed into camphol. But this reaction gives rise to a hydrocarbon $C_{10}H_{16}$, boiling between 170° and 175° C.

$$C_{10}H_{17}Br + \left.\begin{matrix}K\\H\end{matrix}\right\}O = KBr + \left.\begin{matrix}H\\H\end{matrix}\right\}O + C_{10}H_{16}.$$

The acid corresponding to menthol is identical or isomeric with the campholic acid of Delalande, $C_{10}H_{18}O_2$.

The ordinary oxidizing agents, such as nitric acid, chromic acid, &c., do not produce this acid. They at once attack the carbon of the mentholic alcohol. I hope, however, to be able to produce it by a less direct method of oxidation.

VI.—*On some Physical Properties of the Alloys of Tin and Lead.*

By Professor Bolley.

At the Conference of the Chemico-Technical Section of the Swiss Polytechnic School, at the end of the session 1858-9, the following prize problem was offered for solution, the award to be made in May, 1861 :—

1. A survey of all researches hitherto published on the physical properties—especially the hardness, fusibility, and specific gravity, of the alloys of tin and lead.

2. Preparation of *nine* alloys containing definite equivalent quantities of these elements, viz. :—

1 equivalent of tin to $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, 1, $1\frac{1}{2}$, 2, 3, and 4 eq. lead.

3. Determination of the specific gravities and melting points of these alloys; also of their relations as elements of a simple voltaic circuit, in connection with tin, lead, and zinc, and in presence of acids, alkaline liquids, and dilute saline solutions.

The prize was awarded to G. Pillichody, of Bern, from whose Essay we here extract the most interesting results. The experiments were made in the Technological Laboratory of the Institute.

a. Specific Gravity.—From a comparison of the researches of Kupffer, Long, and Thompson, it appears that the specific gravities of the alloys of tin and lead exhibit considerable variation. The author's determinations agree most nearly with those of Long. He found, in accordance with Kupffer, that the specific gravities of these alloys, as determined by experiment, are smaller than the mean values calculated from the quantities and specific gravities of the component metals; but that (contrary to Kupffer's statements) the *expansion*—that is to say, the difference between the observed and calculated densities—is greatest in the alloy SnPb, so that, with an increase in the proportion of either metal, the specific gravities, as determined by experiment and by calculation, approach more nearly to each other.

These relations are exhibited in the following table:—

Specific Gravities of Alloys of Tin and Lead.

	Kupffer.			Long.			Thomson.			Pillichody.			Regnault.
	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	Obs.	Calc.	Diff.	
Sn_4Pb ...	8,1730	8,1826	96	8,188	8,555	367	7,850	8,545	695	8,2347	8,5507	3160	—
Sn_3Pb ...	8,3914	8,3983	69	—	—	—	8,549	9,002	453	8,4087	8,8118	4031	—
Sn_2Pb ...	8,7454	8,7518	64	8,779	9,221	442	8,688	9,209	521	8,7257	9,1954	4697	—
Sn_3Pb_2 ...	—	—	—	—	—	—	—	—	—	9,0377	9,5054	4677	9,387
SnPb	9,4263	9,4366	103	9,460	9,912	452	9,288	9,899	611	9,4330	9,9052	4772	—
Sn_2Pb_3 ...	—	—	—	—	—	—	—	—	—	9,7971	10,2603	4632	—
$SnPb_2$ ...	10,0782	10,3936	154	10,080	10,480	404	—	—	—	10,0520	10,4763	4243	—
$SnPb_3$ ...	10,3862	10,4122	260	—	—	—	—	—	—	10,3311	10,7296	3985	—
$SnPb_4$ ...	10,5551	10,6022	451	10,590	10,875	285	—	—	—	10,5957	10,8686	2729	—

The author's results afford an additional proof that very little dependence is to be placed on the hydrostatic method for the determination of the composition of lead and tin alloys.

b. Melting points.—The statements of different authors respecting the melting points of the alloys of tin and lead, exhibit even greater discordance than those which relate to the specific gravities. Most of those who occupied themselves with the subject prior to the investigations of Rudberg, or without knowledge of those investigations, neglected to observe a very important circumstance, perhaps the most interesting of all, connected with it. This circumstance is easily overlooked, if only the *melting* point be observed, instead of the solidifying point, which gives much more trustworthy results. When the latter method is followed, the thermometer immersed in the melted alloy usually exhibits, during the passage of the mass from the liquid to the solid state, two stationary points. This effect is due to the separation of one or other of the component metals, while an alloy of constant composition still remains liquid. This alloy has the composition Sn_3Pb. An alloy richer in lead would first deposit lead, and an alloy, containing a larger proportion of tin, would first deposit tin—the alloy Sn_3Pb. remaining liquid for a longer or shorter time, and ultimately solidifying at about 181° C. This temperature, therefore, corresponds to the lowest melting

point that can be exhibited by an alloy of tin and lead, a larger proportion of either metal causes the melting point to rise.

Rudberg determined only the intervals of time which elapsed during the fall of temperature through each 10°C. He also employed a thermometer, the zero of which, according to his own statement, had not been exactly determined. Pillichody's experiments, on the other hand, were made with an exact thermometer, and with all the precautions required in observations of this kind. In all these determinations, the constant solidifying point was found to be exactly 181°C.

Table of the Melting Points of Alloys of Tin and Lead.

	Pillichody.	Rudberg.	Thomson.	Kupffer.	Parkes, for
Sn_4 Pb	187	190–180	190	189	(9 Sn + 4 Pb) 173
Sn_3 Pb	181	190–180	182·8	186	(6 + 4) 168·8
Sn_2 Pb	197	210–200	182·8	196	(4 + 4) 188·8
Sn_3 Pb_2	210	—	—	—	—
Sn Pb	235	250–240	182·2	241	(4 + 7) 215·7
Sn_2 Pb_3	246	—	—	—	(4 + 10) 243·3
Sn Pb_2	270	280–290	—	289	(4 + 14) 254·4
Sn Pb_3	283	290–280	—	—	(4 + 22) 269·4
Sn Pb_4	292	—	—	—	(4 + 28) 275

This Table shows that Thomson, who probably also sought for the solidifying point, overlooked the *variable*, and observed the thermometer in the neighbourhood of the *constant* solidifying temperature. Of this constant point, no notice is taken either by Parkes or by Kupffer.

VII.—*New experiments on the Dangers arising from the use of Certain Waters for feeding Steam Boilers.*

By Professor Bolley.

It has hitherto been received, as a kind of dogma in chemico-technical literature, that waters which, when evaporated, deposit

only the *carbonates* of lime and magnesia, are better adapted for feeding steam-boilers than those which likewise yield *sulphate of lime*, because the latter salt, even in small quantity, imparts to the deposit a stony coherence, whereas the carbonates are deposited in the form of a soft mud. That serious mischief may arise from the formation of a stony incrustation on the surface of a boiler is well known, whereas the deposition of merely pulverulent matter has not hitherto been observed to create much inconvenience. Most of the remedies proposed for these evils have likewise for their object the conversion of the sulphate of lime into carbonate; that is to say; the production of a muddy in place of a stony deposit; such for example is the action of carbonate of soda.

Since the practice of heating steam boilers with coal has been introduced into Switzerland, many serious disturbances have been observed in the functions of boilers which were quite unknown so long as they were heated with wood. Both old and new boilers heated from within (the Cornish or Fairbairn construction) have become red-hot at the upper part of the flue near the fire-place, while the water-gauge showed that the level of the water was several inches above the heating surface. The boiler-plates started, and had to be taken out and replaced by new ones, but without any diminution of the evil.

The first of these cases, in which, as well as in the second, I was consulted by the well-known engineering firm of Escher, Wyss, and Co., happened in the Canton Zurich. The water used for feeding the boiler was taken from the Jenabach, on the southern declivity of the Bachtel. Samples from different parts of the stream were sent to me for examination. Three samples were analysed, and yielded the following proportions of solid matter and carbonate of lime :

In 1 litre.	Total solid residue.	Carbonate of lime.
Sample *a*. ..	0·272 grm.	0·2226 grm.
„ *b*. ..	0·2324 „	
„ *c*. ..	0·2426 „	0·2010 „

The water contained very little organic matter; *sulphates were entirely absent;* silica alumma, magnesia, and alkaline salts were present in small quantity only, as compared with the carbonate of

lime. The water may be described as pure, but rather hard—the hardness being of the kind called temporary.

It was suggested that the mischief above mentioned might arise from the circumstance that, above the place at which the water was drawn for feeding the boiler, the refuse water of a bleach-work was discharged into the stream. A bottle of the waste bleaching liquid was, therefore, likewise sent for examination. It contained, in solution, quick lime, chloride of calcium, and a small quantity of decomposed chloride of lime. On mixing it with the water of the stream, a strongly milky turbidity was produced. So far there was nothing that might not have been expected: but at the top of the liquid in the bottle there was a layer of *fatty matter;* which, after mixing with water, solution in ether, and evaporation, remained in the form of a thickish oil. How this comparatively large quantity of fatty matter got into the bleaching liquid could not be ascertained.

The boiler contained a considerable quantity of a whitish *grey pulverulent deposit*, consisting essentially of carbonate of lime. By careful searching, however, certain substances were found in it mechanically mixed; viz.: black scaly particles of iron, ferric oxide, and adhering organic matter, which became perceptible on heating, and red granules, which were found to consist of the remains of a red lead cement. The powder separated from the water exhibited a further peculiarity. When thrown on water, *it swam on the surface, did not become wet, but remained in its place, and dry, even after prolonged boiling.*

A portion of this powder was well dried on the water bath, and then treated with ether, which extracted a small quantity of fatty matter.

The cause of the phenomenon above-mentioned was now apparent. The pulverulent deposit in the boiler completely covered the heated surface of the flue, so that this surface did not come in contact with the water. The quantity of powder in the boiler was so large that it must have formed a layer several inches thick.

The fatty substance which had found its way into the water surrounded the particles of the precipitated carbonate of lime with a layer *which could not be wetted by the water;* and, in consequence of this want of adhesion, the powder was kept floating on the surface. The powder, after being treated with ether and dried,

sank easily under water, and in its original state was easily wetted by alcohol.

The preceding investigations did not, however, afford any precise information as to the nature of the fatty substance. But shortly afterwards, I was made acquainted with another accident of exactly the same kind, which happened to a boiler in the Canton Thurgau. The water with which this boiler was supplied was found to contain, as a means of two experiments, 0·2417 grm. solid matter per litre, 0.045 of which consisted of organic matter, containing traces of nitrogen. The residue from four or five litres of this water was distilled with a slight excess of dilute sulphuric acid: the distillate had a distinct odour of butyric acid.

In this boiler also a considerable quantity of whitish pulverulent matter was deposited, which, so far as I could ascertain, was free from mechanical impurities. This powder also was *not wetted by water*.

On boiling half a pound of it with distilled water, and gradually adding *carbonate of soda*, the powder was at length thrown down to the bottom, and an alkaline liquid was formed, containing the fatty substance in solution. After filtration and concentration, it was mixed with a small quantity of hydrochloric acid; the odour of butyric acid then became perceptible, and small drops of fat were separated, which did not disappear on dilution with water, but, by agitation with ether, and subsequent evaporation, yielded a small quantity of a nearly odourless oily body.

I was, at first, of opinion that the butyric acid might have existed naturally in the water, inasmuch as this acid has been found in many waters derived from peat-bogs; but, on discovering the fat insoluble in water, I abandoned this view, and subsequently learnt from Mr. Jackson, Director of the factory of Escher, Wyss, and Co., that the water supplied to the boiler was taken from the condenser of another steam-engine, and consequently might have derived the fat from that source. It showed, however, scarcely any turbidity; and all the results obtained with it led to the conclusion that the quantity of fat contained in it was very small. Practically, the origin of the fatty matter is of little consequence.

By my recommendation, a small quantity of solution of carbonate of soda was added to the water supplied to the boiler, and by this means the inconvenience above described was completely obviated. It likewise ceased when the water was no longer taken from the condenser of the other engine.

I regard these experiments as well worthy of attention. That observations of such cases, and enquiries into their causes, have been previously published, I have not been able to find. Nevertheless, though various conditions must conspire to produce the result in question, it is very probable that such concurrence frequently takes place.

The results of this investigation may be summed up as follows :—

1. When a boiler is fed with water which deposits only carbonates unmixed with sulphates, the presence of very small quantities of fatty matter may cause the deposit to assume a dusty instead of a muddy consistence. Under such circumstances, rubbing the inside of the boiler with grease can only do mischief.

2. This pulverulent character of the deposit may cause those portions of the boiler-surface which are strongly heated and directly covered by the powder to become red-hot, thereby giving rise to explosions and all their attendant consequences.

3. In such cases, as well as when the water contains sulphates, the addition of a small quantity of carbonate of soda will be found very useful.

4. The effect, so far as regards the form of the deposit, is probably independent of the kind of fuel employed : it appears, however, from the observations hitherto made, that the heating of the boiler plates to redness takes place only when the fires are fed with coal, this kind of fuel producing a more intense heat in the immediate neighbourhood of the burning mass.

VIII.—*On the Construction of Tables exhibiting the Composition and Mutual Relations of Organic Substances.*

By John A. R. Newlands, F.C.S.

These Tables may be formed by arranging all homologous series (whether known or otherwise) in two directions, vertically, according to the difference in the number of equivalents of C and H, and horizontally, according to the number of equivalents of O, contained in the general formula of each series, or *vice versâ*.

The accompanying Table may serve as a specimen of those of a more complete character: it is divided into a number of types, under each of which are placed all substances homologous, or isomeric, with each other.

The following are the principal relations observed on contrasting bodies belonging to these various types:—

I. *Vertically.*

1. Bodies differing by H_2: as $C_5H_{12}O_2''$ amyl-glycol; $C_5H_{10}O_2$ valerianic acid; $C_5H_8O_2$ angelic acid; and $C_5H_6O_2$ picrotoxin.
2. Bodies differing by C: as $C_2H_6O''_2$ ethyl-glycol; $C_3H_6O_2$ propylic acid; $C_4H_6O_2$ crotonic acid; $C_5H_6O_2$ picrotoxin; $C_6H_6O_2$ oxyphenic acid; $C_7H_6O_2$ benzoic acid; and $C_9H_6O_2$ cumarin.
3. Bodies in which C and H_2 replace each other: as $C_4H_8O_2$ butyric acid; $C_5H_6O_2$ picrotoxin; and $C_6H_4O_2$ kinone.
4. Bodies in which C and H_4 replace each other: as butyl-glycol $C_4H_{10}O_2''$; and picrotoxin $C_5H_6O_2$.
5. Bodies differing by CH_4: as $C_7H_6O_2$ benzoic acid; $C_8H_{10}O_2$ terebentilic acid; $C_{10}H_{18}O_2$ campholic acid; and $C_{11}H_{22}O_2$ margaritic acid.

II. *Horizontally.* Bodies differing by O: as C_3H_6'' propylene, C_3H_6O propyl-aldehyde, or allylic-alcohol; $C_3H_6O_2$ propylic acid; $C_3H_6O_3$ lactic acid; and $C_3H_6O_4$ glyceric acid.

III. *Diagonally, from left to right.*

1. Bodies in which O and H_2 replace each other: as C_2H_6O alcohol; $C_2H_4O_2$ acetic acid; and $C_2H_2O_3$ glyoxylic acid.
2. Bodies differing by CO: as CH_4O methylic alcohol, $C_2H_4O_2$ acetic acid; C_3H_4O pyruvic acid; $C_4H_4O_4''$ fumaric acid; and $C_7H_4O_7'''$ meconic acid.

*3. Bodies differing by CO_2. A few of these are here given, from which it may be seen that monobasic, bibasic, and tribasic acids, and also hydrocarbons and alcohols, may be formed from each other by the addition or subtraction of CO_2.

* The diagonal line exhibiting this relation is drawn from the space immediately to the right of a substance; and, in the case marked thus †, from the space immediately to the left. In the remaining instances, the diagonal lines are drawn directly from the substance itself.

Hydrocarbons, alcohols, &c.	Monobasic acids.	Bibasic acids.	Tribasic acids.
H_2 hydride of hydrogen	CH_2O_2 formic acid	$C_2H_2O_4''$ oxalic acid	$C_3H_2O_6'''$
CH_4 ,, methyl	$C_2H_4O_2$ acetic acid	$C_3H_4O_4''$	$C_4H_4O_6'''$
C_2H_6 ,, ethyl	$C_3H_6O_2$ propylic acid	$C_4H_6O_4''$ succinic acid	$C_5H_6O_6'''$
$C_2H_6O_2$ ethyl-glycol	$C_3H_6O_4$ glyceric acid	$C_4H_6O_6''$ tartaric acid	$C_5H_6O_3'''$
CH_4O methylic alcohol	$C_2H_4O_3$ glycolic acid	$C_3H_4O_5$ tartronic acid	$C_4H_4O_7'''$
C_2H_6O ethylic ,,	$C_3H_6O_3$ lactic acid	$C_4H_6O_5''$ malic acid	$C_5H_6O_7'''$
C_3H_8O propylic ,,	$C_4H_8O_3$	$C_5H_8O_5''$	$C_6H_8O_7'''$ citric acid
$C_8H_{10}O_2$	$C_9H_{10}O_4$ everninic acid	$C_{10}H_{10}O_6''$ hemipinic acid	$C_{11}H_{10}O_8'''$
C_2H_4'' ethylene	$C_3H_4O_2$ acrylic acid	$C_4H_4O_4''$ fumaric acid	$C_5H_4O_6'''$ [acid
C_3H_6'' propylene	$C_4H_6O_2$ crotonic acid	$C_5H_6O_4''$ citraconic acid	$C_6H_6O_6'''$ aconitic
C_6H_6 benzol	$C_7H_6O_2$ benzoic acid	$C_8H_6O_4''$ phthalic acid	$C_9H_6O_6'''$
C_7H_8 toluol	$C_8H_8O_2$ toluylic acid	$C_9H_8O_4''$ insolinic acid	$C_{10}H_8O_6'''$
C_4H_4O	$C_5H_4O_3$ pyrocomenic [acid	$C_6H_4O_5''$ comenic acid	$C_7H_4O_7'''$ meconic
C_5H_6O	$C_6H_6O_2$ pyrogallic acid	$C_7H_6O_5''$ gallic acid	$C_8H_6O_7'''$

IV. *Diagonally, from right to left.*

1. Bodies differing by H_2O: as $C_6H_{10}O_8''$ mucic acid; $C_6H_8O_7'''$ citric acid; $C_6H_6O_6'''$ aconitic acid; and $C_6H_4O_5''$ comenic acid.

2. Bodies in which C and O replace each other: as $C_3H_4O_5$ tartronic acid; $C_4H_4O_4''$ fumaric acid; $C_5H_4O_3$ pyrocomenic acid; and $C_6H_4O_2$ kinone.

†3. Bodies in which C and O_2 replace each other: as $C_4H_6O_6''$ tartaric acid; $C_5H_6O''_4$ citraconic acid; and $C_6H_6O_2$ oxyphenic acid.

A table of this sort constitutes, as it were, a map of Organic Chemistry, wherein each substance is surrounded by its derivatives, and those from which it is derivable. Thus, relations between the formulæ of bodies cannot fail to be detected by the most casual observer, many of which might otherwise escape the view of those well acquainted with the science. For instance, the formula of kinic acid $C_7H_{12}O_6''$ is homologous with that of tartaric acid $C_4H_6O_6''$,—a relation which is confirmed by the similarity of their crystals. This suggests the possibility of pimelic acid $C_7H_{12}O_4''$ being formed by the reduction of kinic acid, just as succinic acid $C_4H_6O''_4$ is formed from tartaric, or *vice versâ*. An unknown homologue of malic acid $C_4H_6O_5''$, having the composition $C_7H_{12}O_5''$, might also be produced, and would serve as a connecting link between pimelic and kinic acids.

Other homologous formulæ are,—

...inic acid.....$C_{10}H_8O_6$	Orsellinic acid ...$C_8H_8O_4$	Alpha-orsellic acid $C_{16}H_{14}O_7$	Parellic acid.....$C_9H_8O_4$
...kinic acid $C_{12}H_{12}O_8$	Everninic acid $C_9H_{10}O_4$	Evernic acid.....$C_{17}H_{16}O_7$	Hydropiperic acid $C_{12}H_{12}O_4$

&c., &c.

The principal substitution-product of each substance might be placed beneath it.

Compounds containing nitrogen may be placed in the same Table with non-nitrogenous bodies, by first giving the substances containing C, H, and O only, and afterwards, immediately below, those containing these elements with the addition of one or more atoms of N, P, &c. Or separate tables may be formed of bodies containing carbon, hydrogen, and nitrogen, with their various stages of oxidation. In these, the substances would differ diagonally by CN, NH_3, and the oxides of N.

The mode of classification employed in these Tables has been more or less dilated upon by Messrs. Foster, Schiel, and other chemists; but as I have had them by me now for some years, and none have hitherto been published, I am induced to offer them to the notice of chemists, as a means of suggesting hundreds of reactions, and of showing not only what has been already achieved, but likewise what remains to be accomplished by future researches.

Extract from a Table, exhibiting the Composition and Mutual Relations of Organic Substances. By John A. R. Newlands, F.C.S.

C_nH_{2n+2}	$C_nH_{2n+2}O$	$C_nH_{2n+2}O_2$	$C_nH_{2n+2}O_3$	$C_nH_{2n+2}O_4$	$C_nH_{2n+2}O_5$	$C_nH_{2n+2}O_6$
CH_4 hydride methyl	CH_4O methylic alcohol	CH_4O_2''	CH_4O_3'''	CH_4O_4	CH_4O_5	CH_4O_6
C_2H_6 hydride ethyl	C_2H_6O ethylic alcohol	$C_2H_6O_2''$ ethyl-glycol	$C_2H_6O_3'''$	$C_2H_6O_4$	$C_2H_6O_5$	$C_2H_6O_6$
C_3H_8 hydride propyl	C_3H_8O propylic alcohol	$C_3H_8O_2''$ propyl-glycol	$C_3H_8O_3'''$ glycerin	$C_3H_8O_4$	$C_3H_8O_5$	$C_3H_8O_6$
C_nH_{2n}	$C_nH_{2n}O$	$C_nH_{2n}O_2$	$C_nH_{2n}O_3$	$C_nH_{2n}O_4$	$C_nH_{2n}O_5$	$C_nH_{2n}O_6$
CH_2'' methylene	CH_2O	CH_2O_2 formic acid	CH_2O_3'' carbonic acid	CH_2O_4	CH_2O_5	CH_2O_6
C_2H_4'' ethylene	C_2H_4O aldehyde	$C_2H_4O_2$ acetic ,,	$C_2H_4O_3$ glycolic ,,	$C_2H_4O_4$	$C_2H_4O_5$	$C_2H_4O_6$
C_3H_6'' propylene	C_3H_6O allylic alcohol	$C_3H_6O_2$ propylic ,,	$C_3H_6O_3$ lactic ,,	$C_3H_6O_4$ glyceric acid	$C_3H_6O_5$	$C_3H_6O_6$
C_nH_{2n-2}	$C_nH_{2n-2}O$	$C_nH_{2n-2}O_2$	$C_nH_{2n-2}O_3$	$C_nH_{2n-2}O_4$	$C_nH_{2n-2}O_5$	$C_nH_{2n-2}O_6$
C_2H_2 acetylen	C_2H_2O	$C_2H_2O_2$ glyoxal	$C_2H_2O_3$ glyoxylic acid	$C_2H_2O_4''$ oxalic acid	$C_2H_2O_5$ [acid	$C_2H_2O_6$
C_3H_4	C_3H_4O	$C_3H_4O_2$ acrylic acid	$C_3H_4O_3$ pyruvic ,,	$C_3H_4O_4$	$C_3H_4O_5''$ tartronic	$C_3H_4O_6$
C_4H_6	C_4H_6O	$C_4H_6O_2$ crotonic ,,	$C_4H_6O_3$	$C_4H_6O_4''$ succinic ,,	$C_4H_6O_5''$ malic acid	$C_4H_6O_6''$ tartaric acid
C_nH_{2n-4}	$C_nH_{2n-4}O$	$C_nH_{2n-4}O_2$	$C_nH_{2n-4}O_3$	$C_nH_{2n-4}O_4$	$C_nH_{2n-4}O_5$ [acid	$C_nH_{2n-4}O_6$
C_3H_2	C_3H_2O	$C_3H_2O_2$	$C_3H_2O_3$	$C_3H_2O_4$ [acid	$C_3H_2O_5''$ mesoxalic	$C_3H_2O_6$
C_4H_4	C_4H_4O	$C_4H_4O_2$	$C_4H_4O_3$	$C_4H_4O_4''$ fumaric	$C_4H_4O_5$	$C_4H_4O_6$
C_5H_6	C_5H_6O	$C_5H_6O_2$ picrotoxin	$C_5H_6O_3$	$C_5H_6O_4''$ citraconic [acid	$C_5H_6O_5$	$C_5H_6O_6$
C_nH_{2n-6}	$C_nH_{2n-6}O$	$C_nH_{2n-6}O_2$	$C_nH_{2n-6}O_3$	$C_nH_{2n-6}O_4$	$C_nH_{2n-6}O_5$	$C_nH_{2n-6}O_6$
C_4H_2	C_4H_2O	$C_4H_2O_2$	$C_4H_2O_3$ [acid	$C_4H_2O_4$ mellitic acid	$C_4H_2O_5$	$C_4H_2O_6$
C_5H_4	C_5H_4O	$C_5H_4O_2$	$C_5H_4O_3$ pyrocomenic	$C_5H_4O_4$	$C_5H_4O_5$	$C_5H_4O_6$ [acid
C_6H_6 benzol	C_6H_6O phenylic alcohol	$C_6H_6O_2$ oxyphenic acid	$C_6H_6O_3$ pyrogallic acid	$C_6H_6O_4$	$C_6H_6O_5$	$C_6H_6O_6'''$ aconitic
C_nH_{2n-8}	$C_nH_{2n-8}O$	$C_nH_{2n-8}O_2$	$C_nH_{2n-8}O_3$	$C_nH_{2n-8}O_4$	$C_nH_{2n-8}O_5$	$C_nH_{2n-8}O_6$
C_5H_2	C_5H_2O	$C_5H_2O_2$	$C_5H_2O_3$	$C_5H_2O_4$	$C_5H_2O_5$ croconic acid	$C_5H_2O_6$
C_6H_4 chrysen	C_6H_4O	$C_6H_4O_2$ kinone	$C_6H_4O_3$	$C_6H_4O_4$	$C_6H_4O_5''$ comenic ,,	$C_6H_4O_6$
C_7H_6	C_7H_6O saliretin	$C_7H_6O_2$ benzoic acid	$C_7H_6O_3''$ salicylic acid	$C_7H_6O_4$	$C_7H_6O_5''$ gallic ,,	$C_7H_6O_6$
C_nH_{2n-10}	$C_nH_{2n-10}O$	$C_nH_{2n-10}O_2$	$C_nH_{2n-10}O_3$	$C_nH_{2n-10}O_4$	$C_nH_{2n-10}O_5$	$C_nH_{2n-10}O_6$
C_6H_2	C_6H_2O	$C_6H_2O_2$	$C_6H_2O_3$	$C_6H_2O_4$	$C_6H_2O_5$	$C_6H_2O_6$ [acid
C_7H_4	C_7H_4O	$C_7H_4O_2$	$C_7H_4O_3$	$C_7H_4O_4$ ellagic acid	$C_7H_4O_5$	$C_7H_4O_6'''$ chelidonic
C_8H_6	C_8H_6O	$C_8H_6O_2$	$C_8H_6O_3$	$C_8H_6O_4''$ phthalic ,,	$C_8H_6O_5$	$C_8H_6O_6$